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THERMAL POLYMERIZATION OF STYRENE IN THE PRESENCE OF STABLE
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by

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13. ABSTRACT (Maximum 200 words) Thermal polymerization of styrene in the presence of several radical scavengers and inhibitors was investigated. Rates, molecular weights and polydispersities depend on the nature of the scavenger, on its concentration and reaction temperature. In the best controlled systems, molecular weights up to $M_n \approx 10,000$ and polydispersities $M_w/M_n \approx 1.2$ were observed. It is proposed that in addition to the reversible activation by the homolytic cleavage of the "dormant" [P-R] species, degenerative chain transfer reactions may be involved.				
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THERMAL POLYMERIZATION OF STYRENE IN THE PRESENCE OF STABLE RADICALS AND INHIBITORS

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Introduction

Radical polymerization usually proceeds with slow initiation producing a low stationary concentration of growing radicals, fast propagation with moderate regioselectivity and low stereoselectivity and fast bimolecular termination by recombination or H-abstraction. Recently, we proposed three approaches towards the synthesis of well-defined polymers by radical polymerization¹. They are based on the low stationary concentration of growing radicals and high concentration of chains capable of growth. Some (most) of these chains are, however, in the inactive form. Thus, growing radicals may react reversibly with scavenging radicals to form "dormant" species², or with covalent organometallic compounds to produce stabilized metal-centered radicals³. The third approach employs participation of the growing radicals in the degenerative transfer reactions.

A "living" radical polymerization mechanism was recently proposed in the synthesis of poly(meth)acrylates⁴ and also of low polydispersity polystyrene by initiation with a system involving benzoyl peroxide (BPO) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in various molar ratios at temperatures 125-140 °C^{5,6}. The unusual narrow polydispersities were attributed to the fast initiation by the redox process in which phenyl radicals are formed by TEMPO-promoted decomposition of BPO. Growing polystyryl chains were proposed to be "reversibly" deactivated by scavenging TEMPO radicals, thus, substantially reducing irreversible termination that prematurely stops chain growth. It was assumed that new initiating radicals generated by thermal processes should have no effect on molecular weights and polydispersities. However, at temperatures above 100 °C, "styryl" radicals are continuously produced via thermal initiation process, as long as monomer is present.

In this paper we demonstrate that thermal polymerization of styrene in the presence of TEMPO without any additional radical initiator (peroxide, diazo compound) also produces polymers with narrow molecular weight distribution ($M_w/M_n = 1.15$ to 1.3) and that molecular weights increase linearly with conversion. Various inhibitors have similar effects to nitroxides but act less efficiently.

Results and Discussion

Fig. 1 presents time-conversion plots in semilogarithmic coordinates in thermal bulk polymerization of styrene at 120 °C, at different concentrations of TEMPO.

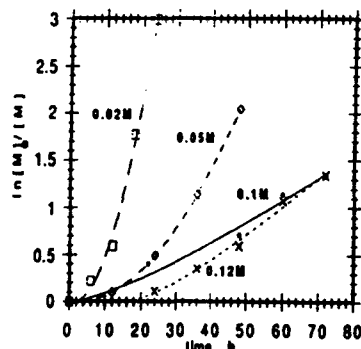


Figure 1 Time-conversion plots in thermal polymerization of styrene, in bulk, 120°C, at different concentrations of TEMPO

Longer induction periods were noticed at higher concentrations of TEMPO which acts as an inhibitor, by scavenging radicals thermally formed until their total consumption. Then, polymerization starts after different induction periods with rates also influenced by the amount of chains capped by alkoxamines.

Dependence of molecular weights (M_n) on conversion is almost linear, the highest values are observed at the lowest concentrations of TEMPO [Fig. 2, (a)].

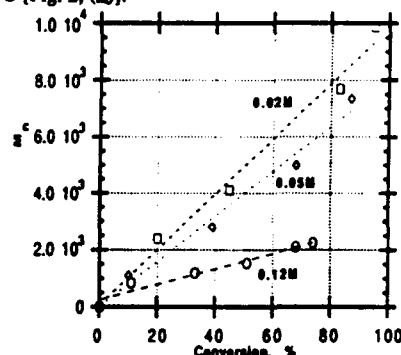


Figure 2 M_n -conversion dependence in polymerization of styrene, in bulk, 120°C, at different concentrations of TEMPO

Polydispersities increase with conversion as shown in Fig. 3. The lowest values ($M_w/M_n = 1.15$ to 1.3) are observed at the highest amount of TEMPO (a).

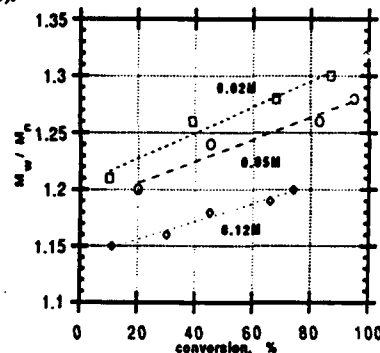


Figure 3 M_w/M_n -conversion plots in thermal polymerization of styrene, 120°C, in bulk, at different concentrations of TEMPO

Temperature has a pronounced effect on polymerization rates, at the same concentrations of TEMPO, (Fig. 4). At higher temperatures (140°C) the highest rates were noticed, but the lowest molecular weights (Fig. 5, (o)), and the lowest polydispersities (Fig. 6, (a)).

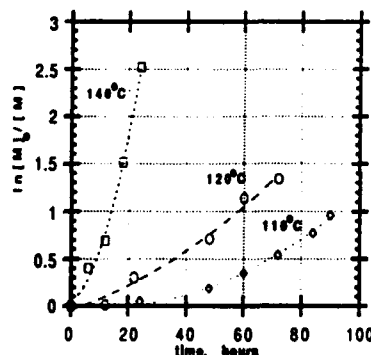


Figure 4 Time-conversion plots in semilogarithmic coordinates in thermal polymerization of styrene, 120°C, at different temperatures. $[TEMPO]_0 = 10^{-1} M$.

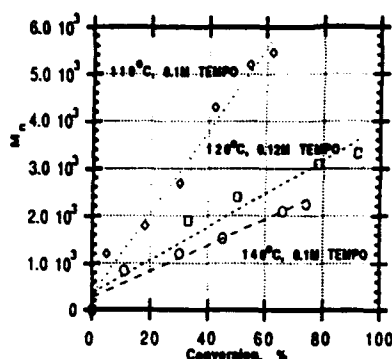


Figure 5 M_n -conversion plots in thermal polymerization of styrene at different temperatures

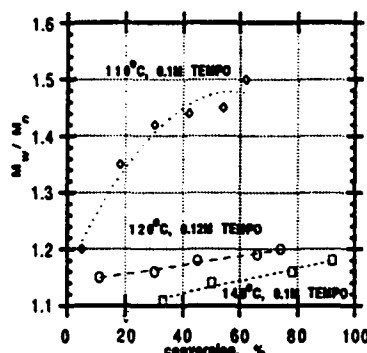


Figure 6 M_w/M_n -conversion dependence in thermal polymerization of styrene at different temperatures and $[TEMPO]_0$

It seems that not only TEMPO but also other stable radicals lead to the substantial decrease of molecular weights and polydispersities in the thermal process. Nitroxyl radicals (like TEMPO) give the best results. However, a classic picryl hydrazyl radical (DPPH), acts in a similar way. Galvinoxyl with a more sterically hindered structure due to the two tert-butyl groups in the ortho position is much less efficient (cf. Table 1)

Table 1 Thermal polymerization of styrene in the presence of different stable radicals, $10^{-1}M$, $T = 120^\circ C$, 48 hours

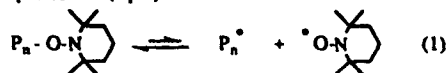
Radical	M_n	M_w/M_n	Conversion %
-	196,000	2.62	87
TEMPO	4,240	1.26	80
4-OH-TEMPO	3,915	1.27	62
4-ox-TEMPO	6,830	1.38	74
2,2,3,4,5,5-Hexamethyl-3-imidazolinium-1-yloxy methyl sulfate	4,367	1.31	78
DPPH	3,444	1.76	36
Galvinoxyl	43,157	1.5	57

Classic inhibitors based on the quinone or phenol structures have much smaller effects but also lead to lower molecular weights and lower polydispersities than in the uninhibited process. (Tab. 2).

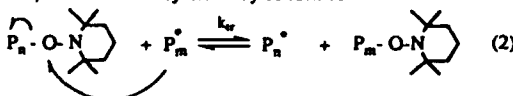
Table 2 Thermal polymerization of styrene in the presence of inhibitors, $120^\circ C$, 22 hours

Inhibitor	M_n	M_w/M_n	Conversion, %
Hydroquinone	61,008	1.7	74
2,6-di- <i>t</i> -butyl-4-methylphenol	110,981	2.07	70
Benzquinone	48,935	1.8	75

The control of molecular weights and decrease of polydispersities was up to now attributed to the reversible homolytic cleavage of the dormant species P-R (eq. 1):



However, it is also possible that radicals formed continuously during thermal initiation may react in the transfer processes with polymeric alkoxyamines. In this thermodynamically neutral process newly generated radicals will react with alkoxyamines (dormant species), reforming radicals of the same structure as growing radicals and alkoxyamines also of the same structure. If the exchange process (degenerative transfer) (eq. 2) is fast enough and the ratio of terminated chains to the total number of chains is low, a well-defined system may be formed.



Conclusions

Thermal polymerization of styrene in the presence of several radical scavengers and inhibitors was investigated. Rates, molecular weights and polydispersities depend on the nature of the scavenger, on its concentration and reaction temperature. In the best controlled systems, molecular weights up to $M_n \sim 10,000$ and polydispersities $M_w/M_n \sim 1.2$ were observed. It is proposed that in addition to the reversible activation by the homolytic cleavage of the "dormant" [P-R] species, degenerative chain transfer reactions may be involved.

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